Determination of polycyclic aromatic hydrocarbons in domestic pellet stove emissions

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ABSTRACT

Biomass is one of the most important renewable energy sources that could help to achieve the 2020 targets set by European Directive 2009/28. This is particularly true in Italy where the government plans to replace a final energy use corresponding to 200–250 PJ through the use of small wood stoves/boilers for domestic heating (<35 kW). This corresponds to about 25% of the national target for 2020. However, this solution is under discussion because of the environmental problems that poses in terms of emissions of PM and PAHs especially in lowland areas. The study, starting from these assumptions, was focussed to better characterize, with laboratory tests, the composition of PAHs emitted by a modern pellet stove and verify their distribution in the solid, liquid and gaseous fractions of the fumes at the stack. In brief, the tests showed that about 85% of the harmful effect of PAH is associated with the PM. This confirms that special attention should be given to the control of the dust through a better design of the stoves and/or the development of abatement equipment also suitable for small devices.

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1. Introduction

Wood combustion for domestic heating is among the main sources of emission of volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) which are linked to harmful effects on human health, such as cardiopulmonary disease and carcinogenic effects and, more in general, with the quality of the air [1–4]. In previous works, mutageniticy of the air in the areas in which the use of wood as fuel is widespread is positively correlated with the PAHs concentration in the air [5]. Moreover, PAHs are generally considered as an important cause of toxicity and mutagenicity of the PM [6,7], they have carcinogenic effects [8] and are strongly persistent and ubiquitous in the environment [9]. The quantity of PAHs in the atmosphere is mainly due to incomplete combustion of fuels based on carbon and hydrogen [10], such as vehicles fuels [11,12] and wood used for space

heating [13–16]. With reference to wood, PAHs emissions depend on many factors like the temperature of combustion, the ratio air/fuel [17] and - in small stoves/boilers - are generally due to the less controlled conditions in which the combustion takes place [18]. According to some Authors, wood combustion could produce more PAHs emissions than any other fuel [19]. A recent survey conducted in Northern Italy [7] showed that, during the cold seasons, wood combustion produces from 30 to 70% of the PAHs associated to the PM_{10} of the ambient air. Emissions are generally higher during the nighttime.

Modern combustion technologies and high quality solid biofuels, like wood pellets, allow a better control of the emissions also in small devices and their widespread use can help to reduce the pollution of the air [18,20]. The use of modern pellet stoves is increasing in Italy and the pellet consumption is increasing from 150 kt in 2001, to 850 kt in 2008 [21] and is estimated at 1.2 Mt in 2009 [22].

Fig. 1 – Sampling Train.

2. Materials and methods

2.1. Pellet stove

The device considered in this work is a top-feed pellet stove with a nominal output of 11.7 kW, manufactured in Italy. The model (mod. 6000AV, Caminetti Montegrappa) is representative of small household heating devices whose size is in the range not yet regulated by the Italian law [31]. The device is similar to that used by Sippula [32]: the fuel storage is embedded in the stove and wood pellets are supplied by a small auger screw to the burner. This is a cast iron cup with holes on the bottom for the passage of the combustion air that is driven by an electric fan. The stove can operate at five levels of power output modifying the pellet and the combustion air flow rates.

2.2. Sampling of PAHs and PM

The stove was installed in the Biomass Laboratory of the Polytechnic University of Marche and was connected to a chimney equipped with a sampling port designed in accordance to EN technical standards [33,34] (Fig. 1). All tests have been performed
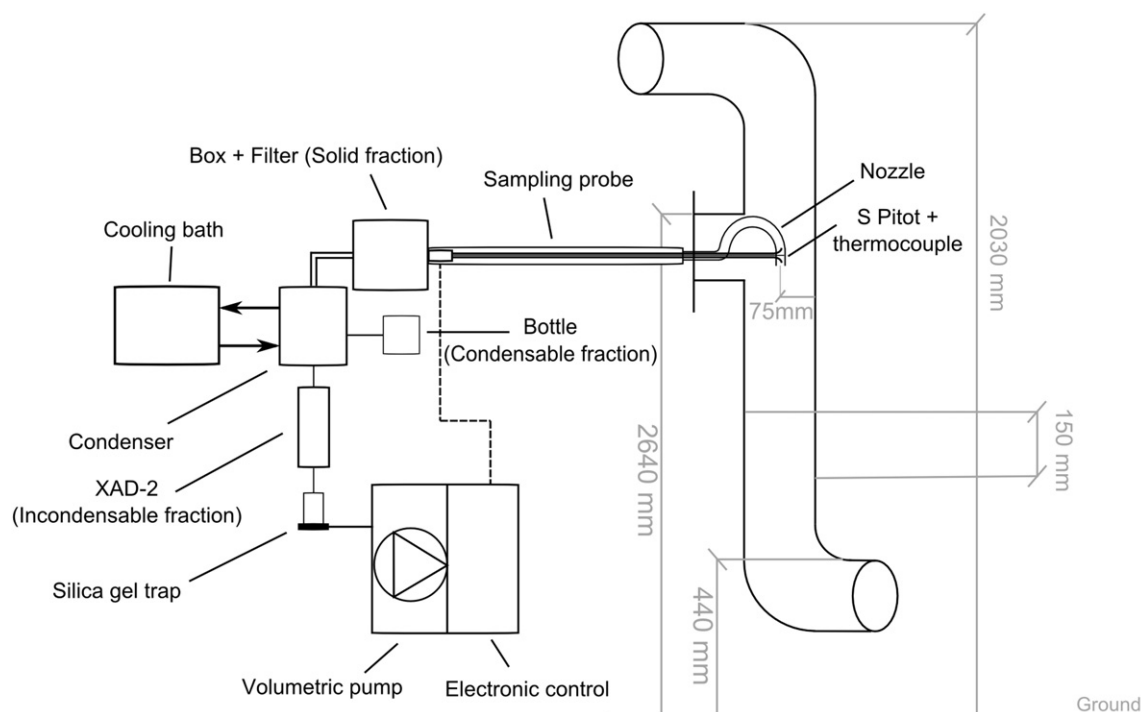
Many studies on the emissions produced by the biomass combustion for domestic heating are available [5,16,19,23–26] but few of them analyze the issue of the PAHs emissions produced by small pellet stove and there are few information about the distribution of the PAHs between the solid phase and the gas phase, which have different carcinogenic effects [27–29].

In Italy, the consumption of wood pellet in small heating devices is also encouraged by the national regulations aiming to foster the utilisation of renewable sources [30] but the environmental issues pose the need for a better understanding of the impact of these technologies and fuels on the environment and human health. In this context, this study aims to give a contribution through the discussion of the emissions of PAHs measured on a pellet stove tested in laboratory.

Table 1 – Pellet stove feed parameters at the two heat output settings studied.

Pellet Stove Parameters	P_{low}	P_{high}
Exhaust blower speed (Hz)	22	26
Feed rate (kg h^{-1})	1.3	2.2
Power (kW fuel input[a])	6.2	10.5

a Calculated according to the net heat value of the pellet as received (17.2 MJ kg^{-1}).
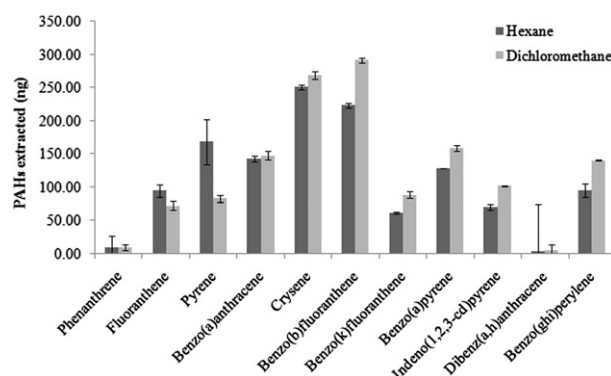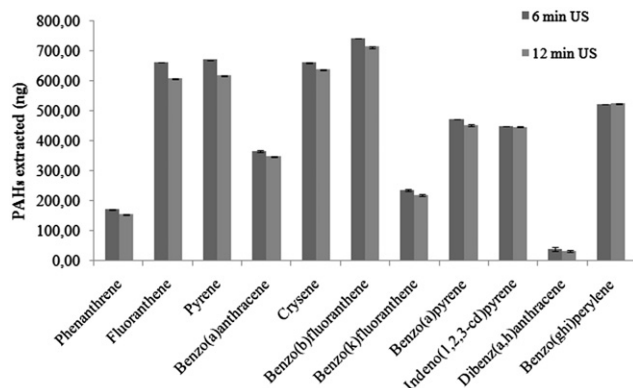

Fig. 2 – Comparison between hexane and DCM (solid fraction). Results obtained from three trials.

Fig. 3 – **Comparison between different time of sonication (solid fraction). Results obtained from three trials.**

with beech pellet, type A compliant to the specification UNI/TS 11263 [35]. The net heat value was of 17.2 MJ kg^{-1}. Each time, before starting the tests, the stove had run for 2 h at fixed power in order to achieve stable conditions of the system. PM and PAHs have been sampled at partial load ($P_{low} = 6.2$ kW fuel input), around 50% of the nominal output, and at full load ($P_{high} = 10.5$ kW fuel input) (Table 1). Tests were repeated three times.

Each sampling lasted an average of 30 min and was performed with an automatic isokinetic sampler (Isostack Basic, Tecora) equipped with a Pitot tube and a thermocouple [33]. An integrated stainless steel AISI 316 probe with an in-stack filter holder 25 mm in diameter (Ministack, Tecora) for PM and a heated titanium probe with a heated out-stack (47 mm) filter holder for PAHs (Tecora), both equipped with quartz microfibre filters without binders (MK-360 Munktell), have been utilized. Samples of PM and PAHs were collected separately to avoid the loss of more volatile compounds during the thermal stabilisation (160 °C) required for the PM collection [33]. Since the PM probe was not heated, the filter was always allowed to reach the exhaust temperature before operation. In this phase, the probe nozzle was directed downstream, to prevent the formation of dust deposits, and was then positioned for sample collection. Particulate was also subjected to a morphological analysis with a scanning electron microscope (SEM). The PAHs sampling instruments were settled in accordance with EN 1948 [36].

Similar sampling equipment has been used in previous works [37,38]. Briefly, the used train includes, besides the probe with the out-stack filter holder box, a counter-current condenser for the collection of the condensable fraction and a XAD-2 sorbent tube (SKC) for the collection of the incondensable fraction (Fig. 1).

After each sampling, the train was rinsed with methanol, to ensure complete analyte recovery [38]. Filters, sorbent tubes and condensable fractions were wrapped in aluminium foil and stored below 4 °C until analysis, which was made within 48 h to prevent photodegradation and/or volatilisation phenomena. Carbon dioxide and oxygen content were measured with a gas analyser (Vario Plus, MRU).

2.3. PAH extraction and analysis

Semivolatile compounds, including PAHs, are present in the different fractions of the stack emissions according to their physical-chemical properties (e.g. molecular weight, vapour pressure, solubility, etc.) [39]. Generally, with reference to the instrumentation described above, the following fractions are found: (i) particulate matter (solid or liquid) carried by the fumes and trapped in the quartz microfibre filter; (ii) condensable fraction, i.e. water and organic substances, which recondense at low temperature in the condenser; (iii) incondensable fraction, consisting of the highly volatile organic compounds that are collected by the adsorbent trap (XAD-2). To extract the PAHs from the particulate fraction (PAH$_{PM}$) and from the incondensable fraction (PAH$_{IN}$), organic solvent extraction and ultrasounds [US] has been used following methods similar to those reported in [37,40,41]. Several solvent types and different sonication times [42–45] have been performed to select the best test materials and procedure. The extracts obtained from each fraction were analyzed by gas chromatography-mass spectrometry (GC-MS; Clarus 600 S, Perkin Elmer) to identify and quantify the 16 PAHs being investigated (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno [1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene).
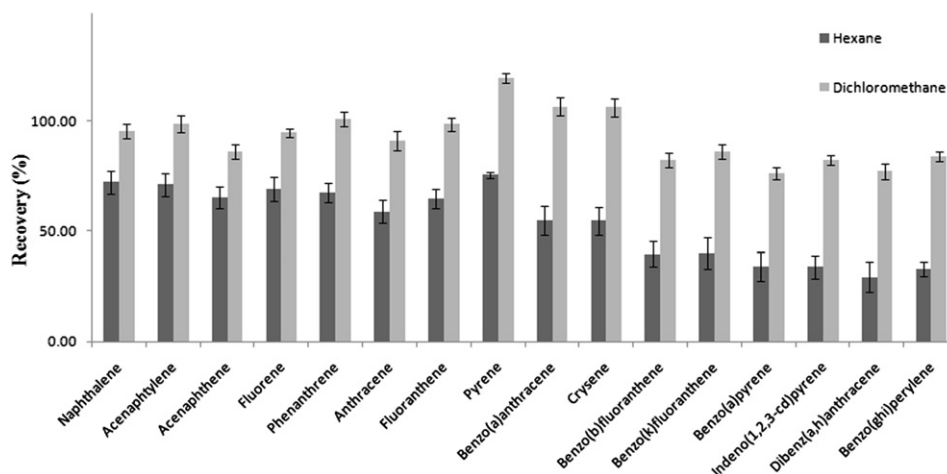
Fig. 4 – **Comparison between hexane and DCM (gaseous fraction). Results obtained from three trials.**
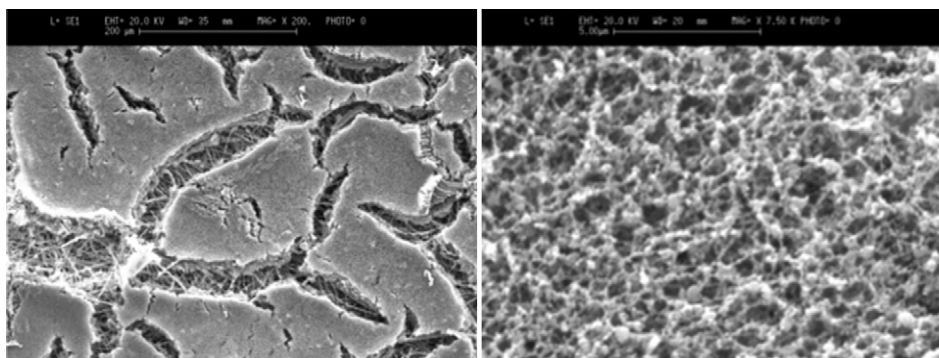
Fig. 5 – Morphological analysis of dusts: left 200X; right 7500X (SEM).

The GC-MS was equipped with a cold on-column injector, a 0.53 mm ID pre-column and a Rxi 5 Sil MS capillary column (30 m × 0.32 mm ID x 0.25 μm film thickness; Restek). The initial oven temperature of 55 °C (2 min) was increased by 15 °C min⁻¹ until 220 °C, then by 2 °C min⁻¹ until 240 °C, and by 15 °C min⁻¹ up to 300 °C, where it was held for 15 min. The initial injector temperature of 60 °C (2 min) was increased by 15 °C min⁻¹ to 235 °C, where it was held for 10 min, then by 15 °C min⁻¹ to 305 °C, where it was held until the end of the analysis. The transfer line and source temperatures were 290 and 230 °C respectively. Helium at a constant flow of 1.5 mL min⁻¹ was used as carrier gas. The mass selective detector was operated in Selected Ion - Full Ion (SIFI) mode: a Total Ion Current (TIC) acquisition was combined with a Selected Ion Monitoring (SIM) acquisition.

The analytes were identified in different ways: (i) by comparing total mass spectra with the National Institute of Standards and Technology (NIST) library; (ii) by comparing mass spectra with the mass spectra of pure PAHs; and (iii) by measuring the relative intensity of the qualifier fragments obtained in SIM mode. The target compounds were quantified in SIM mode. The compounds used as the internal and surrogate standards were: naphthalene-d$_8$, acenaphthene-d$_{10}$, phenanthrene-d$_{10}$, pyrene-d$_{10}$, chrysene-d$_{12}$, and perylene-d$_{12}$. Surrogate standards and internal standards were used to monitor the extraction phase and to enhance the reproducibility of GC-MS analysis, respectively.

Regarding the particulate matter, this sample matrix could not be reproduced and reference material with identical composition is not available, so a portioning filter technique was used to compare different methods of extraction. Thus, samplings of PM from the stove have been carried out and discs (1 cm in diameter) from these filters have been cut to process them using different analytic extraction conditions. For each parameter three analysis were performed and the most effective extraction condition identified by comparison of the amount of PAHs extracted. As extraction solvents,

Table 2 – Characteristics of the flue gas at P_{low} and P_{high}.

Parameter	P_{low}	P_{high}
Flow rate (m³ h⁻¹)	34.6	33.3
Temperature (°C)	143	187
Velocity (m s⁻¹)	0.93	1.01

Table 3 – Absolute values of the emission of PAHs (11% O$_2$) (n = 3).

PAH	P_{low}			P_{high}		
	μg m⁻³		μg MJ fuel input⁻¹	μg m⁻³		μg MJ fuel input⁻¹
	mean	SD		mean	SD	
Naphthalene[1]	60.0	2.8	94.6	54.4	6.7	48.4
Acenaphthylene[2]	13.8	3.9	21.8	8.4	0.9	7.4
Acenaphthene[3]	–	–	–	–	–	–
Fluorene[4]	0.2	0.2	0.3	–	–	–
Phenanthrene[5]	12.2	6.1	19.2	1.0	0.2	0.9
Anthracene[6]	1.2	0.6	1.8	–	–	–
Fluoranthene[7]	15.5	2.6	24.5	3.7	0.2	3.3
Pyrene[8]	10.3	3.5	16.2	2.8	0.6	2.5
Benzo(a)anthracene[9]	–	–	–	0.4	0.1	0.3
Chrysene[10]	0.8	0.1	1.2	1.1	0.3	1.0
Benzo(b)fluoranthene[11]	–	–	–	0.8	0.2	0.7
Benzo(k)fluoranthene[12]	–	–	–	–	–	–
Benzo(a)pyrene[13]	–	–	–	0.4	0.1	0.4
Indeno(1,2,3-cd)pyrene[14]	–	–	–	0.3	0.1	0.2
Dibenz(a,h)anthracene[15]	–	–	–	–	–	–
Benzo(ghi)perylene[16]	–	–	–	0.5	0.1	0.4
ΣPAH[17]	113.9		179.6	73.7		65.6
LMW[a] (%)	76.7			86.6		
MMW[b] (%)	23.4			10.9		
HMW[c] (%)	0.0			2.7		

Notes: - : not detected.
a PAH with low molecular weight (LMW), components with 2–3 rings. $LMW(\%) = \frac{(1+2+3+4+5+6)}{17} * 100$
b PAH with median molecular weight (MMW), components with 4 rings. $MMW(\%) = \frac{(7+8+9+10)}{17} * 100$
c PAH with high molecular weight (HMW), components with 5 or 6 rings. $HMW(\%) = \frac{(11+12+13+14+15+16)}{17} * 100$

hexane and dichloromethane (DCM) - the most used solvents for PAHs extraction [46,47] – have been compared and US applied.

Comparative tests show that DCM performs better than hexane, especially for the extraction of heavy PAHs, usually associated to the PM [27–29]. This solvent permits also to reduce the variance in repetitions, except for the dibenzo(a,h)anthracene (Fig. 2). DCM has proven to be better also for the extraction of PAHs from adsorbent material (XAD-2). The recovery rates of the lightest PAHs – up to crysene – are more than 90% (Fig. 4), while for heavier PAHs are in the region of 75–80%. For these reasons and also for its high volatility, DCM was utilized in all tests. The influence of sonication for solid fraction was also evaluated and a time of 6 min has been chosen (Fig. 3).

PAHs from the condensable fraction (PAH$_{CO}$) were extracted by solid phase extraction (SPE) (Strata-X 33; Phenomenex) [48].

3. Results and discussion

The following average emission factors (11% O_2) of PM were obtained: 132.1 mg m^{-3} (P$_{low}$) and 137.2 mg m^{-3} (P$_{high}$) (in this article m^3 refers to standard pressure and temperature, i.e. 273.15 K and 101.3 kPa). These values are consistent with those described by Johansson (34–240 mg m^{-3}) [26] in small pellet-fuelled combustion devices. In terms of energy (related to the fuel), this corresponds to 208.3 mg MJ fuel input^{-1} (P$_{low}$) and to 122.0 mg MJ fuel input^{-1} (P$_{high}$). Then the PM tends to increase from P$_{high}$ to P$_{low}$. The results of the morphological SEM analysis (Fig. 5) agree with those reported by Johansson [26] since most of the particles size is less than 1 μm. Exposure to ambient PM in general and fine combustion related particles in particular have recently been associated with cardio-pulmonary disease and mortality [20].

The main sampling parameters measured are listed in Table 2; PAH emission values are reported in Table 3.

Also the total PAHs emission depends on the load of the stove: 113.9 μg m^{-3}–179.6 μg MJ fuel input^{-1} for test at P$_{low}$ and 73.7 μg m^{-3}–65.6 μg MJ fuel input^{-1} for test at P$_{high}$ (Table 3). At both heat output settings, the naphthalene was the most abundant PAH (54.4–60.0 μg m^{-3}; 52.7–73.8% of the total), followed by acenaphthylene (8.4–13.8 μg m^{-3}; 11.4–12.1%) and phenanthrene (only for P$_{low}$ 12.2 μg m^{-3}; 10.7%). These results are similar to those obtained by Olsson et al. [49]. Further differences relevant to the quantities of PAHs and their distribution among the different fractions are reported in Table 4. Heavier toxic PAHs are mainly associated to PM (PAH$_{PM}$) and they represent only 11.4–31.7% of the total PAH. Although fewer heavy PAHs are produced at P$_{high}$, the formation of higher molecular weight homologues (benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(123-cd)pyrene and benzo(ghi)perylene) could be noted. These compounds are usually more toxic (Table 5) than others and not detected at P$_{low}$. The lighter PAHs (two–three rings), are predominantly found in the gaseous phase and represent 64–84% of the total.

Table 4 – Relative emission of PAHs in the different fractions.

| PAH | P$_{low}$ | | | | | |
| | PAH$_{PM}$ (%) | | PAH$_{IN}$ (%) | | PAH$_{CO}$ (%) | |
	mean	SD	mean	SD	mean	SD
Naphthalene	0.2	0.1	49.2	8.5	0.1	–
Acenaphtylene	0.4	0.1	10.5	2.0	–	–
Acenaphthene	–	–	–	–	–	–
Fluorene	–	–	0.1	0.2	–	–
Phenanthrene	8.5	1.3	3.9	2.7	0.1	–
Anthracene	0.6	0.1	0.3	0.3	–	–
Fluoranthene	11.6	0.3	0.1	0.1	0.7	0.2
Pyrene	9.9	0.3	0.1	0.1	0.3	0.1
Benzo(a)anthracene	–	–	–	–	–	–
Crysene	0.5	0.1	–	–	0.1	–
Benzo(b)fluoranthene	–	–	–	–	–	–
Benzo(k)fluoranthene	–	–	–	–	–	–
Benzo(a)pyrene	–	–	–	–	–	–
Indeno(1,2,3-cd)pyrene	–	–	–	–	–	–
Dibenz(a,h)anthracene	–	–	–	–	–	–
Benzo(ghi)perylene	–	–	–	–	–	–
ΣPAH	31.7		64.3		1.4	
PAH (%)	P$_{high}$					
	PAH$_{PM}$ (%)		PAH$_{IN}$ (%)		PAH$_{CO}$ (%)	
	mean	SD	mean	SD	mean	SD
Naphthalene	0.1	0.1	72.1	4.0	0.3	–
Acenaphtylene	–	–	11.8	2.8	0.6	–
Acenaphthene	–	–	–	–	–	–
Fluorene	–	–	–	–	–	–
Phenanthrene	0.2	–	0.3	0.1	0.6	0.2
Anthracene	–	–	–	–	–	–
Fluoranthene	3.6	1.5	–	–	0.4	0.1
Pyrene	3.0	1.3	–	–	0.4	0.1
Benzo(a)anthracene	0.5	0.1	–	–	–	–
Crysene	1.6	0.2	–	–	–	–
Benzo(b)fluoranthene	1.1	0.2	–	–	–	–
Benzo(k)fluoranthene	–	–	–	–	–	–
Benzo(a)pyrene	0.5	0.1	–	–	–	–
Indeno(1,2,3-cd)pyrene	0.3	0.1	–	–	–	–
Dibenz(a,h)anthracene	–	–	–	–	–	–
Benzo(ghi)perylene	0.5	0.2	–	–	–	–
ΣPAH	11.4		84.2		2.4	

Notes: - : not detected.

Table 5 – Toxic equivalence factors (TEF) according to Nisbet and LaGoy [52].

PAH	TEF
Naphthalene	0.001
Acenaphthylene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Anthracene	0.01
Fluoranthene	0.001
Pyrene	0.001
Benzo(a)anthracene	0.1
Chrysene	0.01
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.1
Benzo(a)pyrene	1
Indeno(1,2,3-cd)pyrene	0.1
Dibenz(a,h)anthracene	1
Benzo(ghi)perylene	0.01

Table 6 – Values of TEQ calculated according to the results of the trials.

TEQ	P_{low}	P_{high}
TEQ_{tot} (µg MJ fuel input^{-1})	0.21	0.56
TEQ_{PM} (µg MJ fuel input^{-1})	0.08	0.49
TEQ_{PM}/TEQ_{tot} (%)	36.7	86.4

This is in line with the findings of other Authors [38]. Some polycyclic hydrocarbons are found in a single phase; others, like phenanthrene, are associated both with the gaseous and the solid phase.

In addition, at P_{low}, 31.7% of PAHs are found in the solid phase and the 64.3% in the gaseous phase. Similarly, at P_{high}, 11.4% of PAHs are found in the solid phase and 84.2% in the gaseous one. Moreover, the condensable fraction generally represents a very low part of the total PAH, always less than 3%.

Several PAHs compounds have been classified as probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer [50]. The carcinogenic effect associated with the exposure to PAHs can be expressed in terms of "toxicity equivalent" (TEQ) calculated assigning to each single PAH a reference value for toxicity or "BaP- based toxicity equivalent factor" (TEF). The TEQ value is calculated as the sum, extended to all the detected compounds, of the products between concentrations and TEFs [51]. With reference to the most utilized reference values for TEFs, shown in Table 5, the estimated TEQ is 0.21 µg MJ fuel input^{-1} and 0.56 µg MJ fuel input^{-1} respectively for P_{low} and P_{high}. However, more than 85% of the total TEQ (P_{high}) (Table 6) is associated with PM because the more toxic PAHs are present in this fraction.

4. Conclusions

The levels of PAHs vary between around 66 and 180 µg MJ fuel input^{-1} depending mainly on the load of the stove that affects also their distribution in the different fractions (solid, liquid and gaseous). As the load of the stove increases, the PAHs are mostly found in the incondensable fraction and increase also their average molecular weight. In addition:

- the compounds in the incondensable fraction are characterized by two or three rings, and are considered less harmful;
- those in the condensable fraction are small part of the total (always under 3%);
- those associated to PM are the more harmful, as they incorporate the largest share in terms of TEQ.

In conclusion, the way forward to reduce emissions of PAHs of small stoves – apart the optimization of the combustion of the fuel – is mainly linked to the reduction of PM. Therefore it is necessary to develop the design of the stoves so as to minimize such emissions or provide for additional devices (filters or other) to achieve the same goal.

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